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<p>(21) International Application Number: PCT/US98/26019 (22) International Filing Date: 8 December 1998 (08.12.98) (30) Priority Data: 08/987,898 10 December 1997 (10.12.97) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: HALLING, Robert, Allen; 2713 Keswick Court, Wilmington, DE 19808 (US). TAKAHASHI, Tatsuhiro; Solitaire-U #302, 4-16-17, Ikenohata, Taitou-ku, Tokyo 110-0008 (JP). IWATO, Satoko; 4-27-8, Jingumae, Shibuya-ku, Tokyo 150 (JP). (74) Agent: TOCKER, Edwin; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p>		<p>(81) Designated States: CN, JP, KR. Published <i>With international search report.</i></p>
<p>(54) Title: FLUOROCARBON SILANE HYDROLYSATE-CONTAINING AQUEOUS EMULSIONS, AND MATERIALS COATED THEREWITH (57) Abstract Aqueous emulsions containing 1) a fluorocarbon silane hydrolysate generated in the presence of a surfactant and 2) a silicate, which provides a clear and smooth coated surface having excellent water repellency and heat resistance when applied to a substrate are disclosed as well as materials coated therewith.</p>		

FLUOROCARBON SILANE HYDROLYSATE-CONTAINING
AQUEOUS EMULSIONS, AND MATERIALS COATED THEREWITH

FIELD OF THE INVENTION

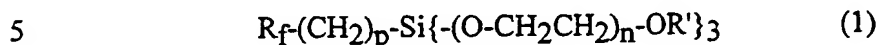
5 The present invention relates to fluorocarbon silane hydrolysate-containing aqueous emulsions. More specifically, it relates both to fluorocarbon silane hydrolysate-containing aqueous emulsions which, when coated and dried on a substrate, are able to provide a water-repelling surface that is clear, smooth, and has an improved heat resistance; as well as to materials obtained by coating and
10 drying this aqueous emulsion on the surface of a substrate.

BACKGROUND OF THE INVENTION

 Various proposals have been made concerning silane-containing aqueous solutions that are capable of conferring water and oil repellency to the surface of substrates. A method has been developed (Japanese Kokai No. 4-338,137 [1992])
15 that uses a solution obtained by mixing a silicon alkoxide having the formula $\text{Si}(\text{OR})_4$, a substituted silicon alkoxide in which some of the alkoxyl groups have been substituted with fluoroalkyl groups, an alcohol, water, and an acid or a base in order to produce water-repellent glass by forming a water-repellent clear film on the surface of a glass substrate. However, this has the drawback that a high
20 concentration cannot be achieved because silicon alkoxide which has been partially substituted with fluoroalkyl groups does not readily dissolve in an alcohol/water-type solvent. Moreover, because this aqueous solution consists of a silicone alkoxide- and alcohol-containing solution in which an acid or a base has been included, the reaction proceeds over time, during the course of which the
25 viscosity rises; hence, the storage stability is poor. In addition, the fact that alcohol is used makes this method environmentally undesirable.

 U.S. Patent 5,550,184 discloses emulsions of hydrolyzable alkoxysilane compounds which are able to confer water and oil repellency to a substrate without requiring a special curing operation. However, although these emulsions

The fluorocarbon silane hydrolysate-containing aqueous emulsions according to the present invention for resolving the above-described problems contain at least one hydrolysate of a fluorocarbon silane having the formula



wherein R_f is a perfluoroalkyl group having from 3 to 18 carbon atoms, or a mixture thereof; each R' is independently an alkyl group having from 1 to 3 carbon atoms; p is from 2 to 4; and n is from 2 to 10, said hydrolysate generated in the presence of a surfactant, and a silicate having the formula



wherein each R is independently selected from the group consisting of OCH_3 , OCH_2CH_3 and $(OCH_2CH_2)_mOCH_3$ wherein m is 1 to 10.

The fluorocarbon silane hydrolysate-containing aqueous emulsions according to the present invention are those in which the content of the
15 fluorocarbon silane in the aqueous emulsion is from 0.1 to 20% by weight, and the molar fraction of the silicate with respect to the fluorocarbon silane is from 0.3 to 10. Two or more hydrolyzed fluorocarbon silanes may be mixed and used together.

In the aqueous emulsions of the present invention, use is made of, from
20 among hydrolyzable alkoxysilane compounds, those fluorocarbon silanes where R_f is a perfluoroalkyl group having from 3 to 18 carbon atoms. These are preferably perfluoroalkyl groups in which R_f represents mixed perfluoroalkyl groups having an average of from 3 to 12 carbon atoms. R' is a C_1 - C_3 alkyl. Preferably R' is methyl, p is 2, and n is from 2 to 4. When n is 2, the preferable
25 fluorocarbon silane hydrolysates are hydrolysates of perfluoroalkylethyltris(2-(2-methoxyethoxy)ethoxy)silanes; when n is 3, the preferable fluorocarbon silane hydrolysates are hydrolysates of 2-perfluoroalkylethyltris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-silanes. This type of fluorocarbon silane is produced by known methods. See Kirk-Othmer, Encyclopedia of Chemical

present invention. Emulsions are achieved by emulsifying the hydrolyzable
alkoxysilane in water in the presence of an effective amount of surfactant of
sufficiently high HLB value to simultaneously retain said hydrolyzable
alkoxysilane compound in a substantially totally hydrolyzed state and inhibit said
5 resulting hydrolyzed alkoxysilane compound from self-condensation. Surfactants
suitable for use herein are chosen from nonionic, cationic, anionic and amphoteric
types. Preferred surfactants are those that have an HLB ("The HLB System"
published by ICI America's Inc., Wilmington, Del.; Adamson, A. W., "Physical
Chemistry of Surfaces," 4th. Ed., John Wily & Sons, N.Y., 1982, p. 475) value
10 greater than 12, and preferably greater than 16. Surfactants with HLB values from
12 to 16 may be used, but, usually require significantly greater quantities to
achieve emulsions of adequate stability. Mixtures of emulsifiers that each meet
the above HLB requirements may be used if they are compatible with one another.
Suitable emulsifiers include, but are not limited to, alkylbenzenesulfonates, linear
15 alkyl diphenyletherdisulfonates, alpha-olefin sulfonates, ethoxylated alkyl alcohol
ethers, ethoxylated alkyl alcohol ether sulfates, ethoxylated alkylphenols,
ethoxylated alkylphenol ether sulfates, ethoxylated perfluoroalkylalkanols, C₈-18
alkyltrimethylammonium salts, C₈-18 alkyl dimethylammonium salts, ethoxylated
C₈-18 amine salts, and alpha-trimethylamino fatty acid betains and perfluoroalkyl
20 amphoteric surfactants of the type $R_f-CH_2CH(OR'')CH_2N(CH_3)_2CH_2CO_2$ (inner
salt) where R'' is H or acetyl, and quaternary salts of the type
 $R_f-CH_2CH_2SCH_2CH(OH)CH_2N(CH_3)_3^+Cl^-$.

Specific examples that are suitable include nonionic surfactants such as
 $R_f-CH_2CH-O-(CH_2CH_2O)_{11}-H$, or $C_9H_{19}-C_6H_4-O-(CH_2CH_2O)_{50}-H$; cationic
25 surfactants such as $R_f-CH_2CH_2SCH_2CH(OH)CH_2N(CH_3)^+Cl^-$, and anionic
surfactants such as $C_{12}H_{25}(OCH_2CH_2)_4OSO_3^-NH_4^+$ and $C_{12}H_{27}-C_6H_4-$
 $SO_3^-Na^+$. The R_f in the above surfactants is a perfluoroalkyl group, usually
having 3 to 18 carbon atoms. After the aqueous emulsion has been applied to the
substrate and dried, it is preferable that the hydrophilic portion within the
30 chemical structure of the surfactant be lost due to heat aging. Because the

In order to obtain a stable aqueous emulsion, the ratios in which the ingredients are included within the aqueous emulsion are set as desired while taking into account all of these conditions.

5 Some desirable examples of stable aqueous emulsions, in cases where a nonionic surfactant represented by the formula $R_f-CH_2CH_2-O-(CH_2CH_2O)_{11}-H$ is used, are aqueous emulsions in which 1) the fluorocarbon silane content is from 0.1 to 20% by weight, the molar fraction of silicate with respect to fluorocarbon silane is from 0.1 to 0.5, and the pH has been adjusted to less than 4, and in particular to from 2 to 3, and the weight ratio of fluorocarbon silane and surfactant used to generate the hydrolysate is from 1:1 to 10:1; 2) aqueous emulsions in which the fluorocarbon silane content is from 0.1 to 1.0% by weight, the molar fraction of silicate with respect to fluorocarbon silane is from 0.1 to 1, the pH has been adjusted to less than 4, and in particular to from 2 to 3, and the weight ratio of the fluorocarbon silane and the surfactant used to generate the hydrolysate is from 1:1 to 10:1; 3) aqueous emulsions in which the fluorocarbon silane content is from 0.1 to 2.5% by weight, the molar fraction of silicate with respect to fluorocarbon silane is from 0.1 to 1, the pH has been adjusted to from 4 to 7, and the weight ratio of the fluorocarbon silane and the surfactant used to generate the hydrolysate is from 1:1 to 10:1; and 4) aqueous emulsions in which the fluorocarbon silane content is from 0.1 to 20% by weight, the molar fraction of the silicate with respect to the fluorocarbon silane is from 0.1 to 5, the pH has been adjusted to 7 or more, and the weight ratio of the fluorocarbon silane and the surfactant used to generate the hydrolysate is from 1:1 to 10:1.

25 In cases where a nonionic surfactant represented by the formula $C_9H_{19}-C_6H_4-O-(CH_2CH_2O)_{50}-H$ is used, as long as an aqueous emulsion is used that has a fluorocarbon silane content of from 0.1 to 20% by weight, a silicate molar fraction with respect to fluorocarbon silane of from 0.1 to 5, and a weight ratio of fluorocarbon silane to surfactant used to generate the hydrolysate is from 1:1 to 10:1, this may have any pH.

The aqueous emulsions of the present invention are applied and dried on a substrate such as a polymer substrate having pendant active hydrogen groups, such as polyesters and polyamides, wood, brick, concrete, stone, glass, ceramic tiles, aluminum sheet, stainless-steel sheet, natural and synthetic fibers, leather and like.

Application of the aqueous emulsion onto the substrate is carried out by a known method such as dipping, spraying or spin coating. In cases where the aqueous emulsion is applied onto a glass substrate, a dipping method is preferable so as not to lose the clarity. Heating may also be carried out in order to accelerate the drying step. Drying is generally carried out for 1 to 24 hours within a temperature range of from 100 to 300°C. Where necessary, the substrate onto which the aqueous emulsion has been applied and dried is washed with water after it has dried, thereby removing the remaining surfactant.

The aqueous emulsions of the present invention are useful in providing oil and water repellant surfaces when coated and dried on a substrate. The coated surface is clear, smooth, and has excellent heat resistance. The coated substrates are useful in situations where the glass, fabrics, construction materials, and polymeric surfaces require oil and water repellency and clear coatings.

EXAMPLES

The aqueous emulsion of the hydrolysate of the fluorocarbon silane and the surfactant were prepared as in U.S. 5,550,184 wherein the fluorocarbon silane was emulsified in water with an effective amount of the indicated surfactant to retain the fluorocarbon silane in a substantially totally hydrolyzed state. Additional components were added to the emulsions as depicted in the examples below.

WORKING EXAMPLES 1-7

The fluorocarbon silane hydrolysate used was a hydrolysate of a compound having the formula $R_f-(CH_2)_2-Si\{-(O-CH_2CH_2)_2-OCH_3\}_3$ wherein R_f is a mixed perfluoroalkyl of formula $F(CF_2)_kCH_2CH_2-$ having the following

obtained.

Water Repellency

A drop of pure water was added to the surface of the coated substrate, and the contact angle was measured with a contact angle analyzer (manufactured by Kyowa Kaimen Kagaku).

The stability of the aqueous emulsion, and the clarity and water repellency of the coated surface are each shown in Table 1 below.

Comparative Example A

In Comparative Example 1, an aqueous emulsion containing no silicate but containing the fluorocarbon silane of working Examples 1-7 was prepared. Using the aqueous emulsion thus obtained, test pieces were fabricated and tested in the same manner as in Working Examples 1-7. The stability of the aqueous emulsion, and the clarity and water repellency of the coated surface are given in Table 1.

Table 1

Example	Working Ex. 1	Working Ex. 2	Working Ex. 3	Working Ex. 4	Working Ex. 5	Working Ex. 6	Working Ex. 7	Comp. Ex. A
Type of silicate	TEOS	Si(DEGM) ₄	TEOS	TEOS	TEOS	TEOS	TEOS	—
pH of aqueous emulsion	2.0	2.0	2.0	2.9	3.0	2.0	2.0	2.0
Fluorosilane concentration (wt %)	10	10	10	10	10	15	2.5	10
Molar fraction	0.5	0.5	0.25	0.33	1.0	0.5	0.5	—
Stability	stable	stable	stable	stable	somewhat unstable	stable	stable	stable
Substrate	glass	glass	glass	glass	glass	glass	glass	glass
Clarity	clear	clear	slightly cloudy	clear	clear	clear	clear	somewhat cloudy
Water-repelling angle (degrees)	113	113	110	110	110	110	110	107
Water-repelling angle (°) after 100 hours at 300°C	113	113	—	—	—	—	—	99
Water-repelling angle (°) after 15 hours at 350°C	73	73	—	—	—	—	—	29

As in Working Example 2, the fluorocarbon silane hydrolysate used was a hydrolysate of a compound having the formula $R_f(CH_2)_2-Si\{-(O-CH_2CH_2)_2-OCH_3\}_3$, the silicate was tetrakis [2-(2-methoxyethoxy)ethyl]silicate

- 5 (Si(DEGM)₄), and the surfactant was a nonionic surfactant having the formula $R_f-CH_2CH_2-O-(CH_2CH_2O)_{11}-H$. As in Working Example 2, the content of surfactant within the aqueous emulsion was set at 30 parts by weight per 100 parts by weight of fluorocarbon silane. The pH was rendered alkaline by using ammonia water. The stability of the aqueous emulsion thus prepared was
- 10 examined in the same manner as in Working Example 2, and application of the aqueous emulsion as well as observation of the clarity and water repellency of the coated surface were carried out in the same manner as in Working Example 2. The results are presented in Table 2.

Comparative Examples B and C

- 15 In Comparative Examples B and C, aqueous emulsions containing no silicate but containing the fluorocarbon silane hydrolysate of working Examples 8-9 were prepared. Using the aqueous emulsion thus obtained, test pieces were fabricated in the same manner as in Working Examples 8 and 9. The stability of the aqueous emulsion, and the clarity and water repellency of the
- 20 coated surface are shown in Table 2.

Example	Working Example 10	Comparative Example D
Type of silicate	Si(DEGM) ₄	—
pH of aqueous emulsion	2.0	2.0
Fluorosilane concentration (wt %)	10	10
Molar fraction	0.5	—
Stability	stable	stable
Substrate	glass	glass
Clarity	very slightly cloudy	somewhat cloudy
Water-repelling angle (degrees)	108	104
Water-repelling angle (°) after 5 hours at 350°C	57	37

From this it was apparent that even when another nonionic surfactant was used, the clarity due to silicate addition was enhanced and the heat resistance was also enhanced.

5 Working Example 11, Comparative Example E

In Working Example 11 and Comparative Example E, aside from replacing the surfactant used in Working Example 2 and Comparative Example A with a cationic surfactant having the formula $R_f-CH_2CH_2SCH_2CH(OH)CH_2N(CH_3)_3Cl$, the aqueous emulsions were prepared, the stability was observed, and the clarity and water repellency of the coated surfaces were examined, all in the same manner as in Working Example 2 and Comparative Example A, respectively. The results are given in Table 4.

Table 5

Example	Working Example 12	Comparative Example F
Type of silicate	Si(DEGM) ₄	—
pH of aqueous emulsion	2.0	2.0
Fluorosilane concentration (wt %)	10	10
Molar fraction	0.5	—
Stability	stable	stable
Substrate	glass	glass
Clarity	clear	somewhat cloudy
Water-repelling angle (degrees)	107	107
Water-repelling angle (°) after 5 hours at 350°C	37	20

Working Example 12 showed that even when an anionic surfactant was used, the clarity and heat resistance were enhanced by the addition of silicate.

Working Examples 13-15, Comparative Example G

- 5 In Working Examples 13-15 and Comparative Example G, aside from using a stainless-steel sheet (2.5 x 5.0 cm, 1-mm thick) instead of the glass plate in Working Example 2 and Comparative Example A, the aqueous emulsions were prepared and observations were carried out in the same manner as in Working Example 2 and Comparative Example A, respectively. The results are given in
- 10 Table 6. The grades of the stainless steel used in the working examples and the comparative example are indicated in the table.

Example	Working Example 16	Comparative Example H
Type of silicate	Si(DEGM) ₄	—
pH of aqueous emulsion	10.8	10.8
Fluorosilane concentration (wt %)	10	10
Molar fraction	0.5	—
Stability	stable	stable
Substrate	aluminum	aluminum
Clarity	clear	film adhesion was poor
Water-repelling angle (degrees)	113	101
Water-repelling angle (°) after 100 hours at 300°C	—	—
Water-repelling angle (°) after 5 hours at 350°C	123	13

Even when the substrate was aluminum, it was apparent that the addition of silicate enhances the clarity and also enhances the heat resistance.

Effects of the Invention

5 As explained above, coated surfaces obtained by coating and drying the fluorocarbon silane hydrolysate-containing aqueous emulsions of the present invention onto a substrate were clear and smooth, and were able to provide excellent water repellency and heat resistance. In addition, by adjusting both the molar ratio of fluorocarbon silane hydrolysate and silicate within the aqueous emulsion and the pH according to the type of surfactant used, stable aqueous emulsions having good storability were obtained.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 513 727 A (TOYOTA) 19 November 1992 &JP04338137 (D) see claim 1	1
A	US 5 552 476 A (HALLING) 3 September 1996 &US5550184 (D) see claim 1	1

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Lentz, J

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